

[Regular Paper]

Effect of Micropore Size on Catalyst Deactivation in Vapor Phase Beckmann Rearrangement over Zeolites

Takeshige TAKAHASHI*, Mayumi NAKANISHI, and Takami KAI

Dept. of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University,
Korimoto 1-21-40, Kagoshima 890-0065, JAPAN

(Received January 16, 2006)

The vapor phase Beckmann rearrangement of cyclohexanone oxime (CHO) was carried out over TS-1 with an MFI pore structure and SSZ-31 and SSZ-24 with pore sizes larger than that of MFI to elucidate the effect of the pore size on catalyst deactivation. The deactivation constant over SSZ-24 was the highest among the zeolites used in the study. Furthermore, when the ratio between the molecular size of ϵ -caprolactam (CL) and the pore size of zeolite was unity, the deactivation constant was maximum over the zeolites at similar acidity. These results indicate that since CL produced on the active sites cannot diffuse from the micropores, the CL reacts to form coke or its precursor over a long residence time. The pore size of the zeolite is the main controlling factor of catalyst deactivation during the Beckmann rearrangement.

Keywords

Beckmann rearrangement, Cyclohexanone oxime, Zeolite, Caprolactam selectivity, Catalyst deactivation, Pore size effect

1. Introduction

The vapor phase Beckmann rearrangement of cyclohexanone oxime can be carried out over many types of zeolites or related solid catalysts, such as high silica MFI zeolite^{1~3)}, TS-1⁴⁾, β -type zeolite^{5),6)}, SAPO-11⁷⁾, meso-porous materials⁸⁾ or layered silicates⁹⁾. The rearrangement can also be performed over amorphous solid acid catalysts such as silica-alumina¹⁰⁾, alumina and silica supported boria^{11),12)}, boria supported on TiO₂-ZrO₂¹³⁾ and tantalum oxide supported on silica¹⁴⁾. The selectivity for ϵ -caprolactam (CL) over these amorphous catalysts is up to 90% under various reaction conditions. The catalyst life determined as the half-life, defined as the time at which rate constant becomes half of the initial value, does not exceed 100 h. On the other hand, the CL selectivity and half-life period over high silica HZSM-5 exceeds 95% and 2000 h, respectively. The reaction mechanism involving nest silanols, in the rearrangement proposed by Hoeldlich *et al.*^{15),16)}, is widely accepted. Furthermore, the theoretical approach to the reaction mechanism reveals that hydrogen bonding of the Si-OH group of the nest silanols to cyclohexanone oxime (CHO) is the initial step of the rearrangement¹⁷⁾.

High silica MFI zeolite without acidity may be the

most suitable catalyst for the vapor phase Beckmann rearrangement¹⁸⁾. Sumitomo Chemical Co., Ltd. in Japan constructed the first plant using the vapor phase Beckmann rearrangement in 2002. A fluidized bed catalytic reactor was adopted in the plant, because the catalyst deactivation rate is too high to use the catalyst for a fixed bed reactor.

Catalyst deactivation of the Beckmann rearrangement is responsible for adsorption of the coke precursor, such as the oligomer of the CL, based on analysis of high molecular components of the products^{19),20)}. The micropore size of the catalysts also affects the catalyst deactivation based on comparison of the reactions over MFI type zeolite and amorphous silica alumina catalyst²¹⁾. However, the micropore distributions of the MFI type zeolite and silica alumina catalyst are different.

In the present study, the rearrangement was carried out over a high silica TS-1 zeolite with the MFI structure, and HZSM-5, SSZ-31 and SSZ-24 zeolites to elucidate the effect of the micropore size on the CL selectivity and catalyst deactivation rate. The deactivation rates obtained over chabazite, mordenite and HY zeolite were included to consider the effect of the micropores. The coke content after the rearrangement of the used catalyst was also determined to clarify the deactivation mechanism of the Beckmann rearrangement.

* To whom correspondence should be addressed.

* E-mail: takahashi@cen.kagoshima-u.ac.jp

Table 1 Properties of Zeolite Used in This Study

Code name	Zeolite	Si/Ti ratio ^{a)}	Acidity [mmol/g]	S.A ^{b)} [m ² /g]	Pore size [nm]
MFI	TS-1(45)	45	0.055	400	0.54 × 0.56
	TS-1(90)	90	0.016	420	
	TS-1(200)	200	0.0092	380	
	TS-1(300)	300	0.0040	410	
—	ZSM-5	Si/Al = 90	0.38	390	0.57 × 0.86
	SSZ-31	Si/Al = 962	0.026	330	
AFI	SSZ-24	Si/Al = 90	0.022	290	0.73

a) Si/Ti ratio was calculated from the starting gel solution. b) Specific Surface Area.

2. Experimental

High silica SSZ-31 (Si/Al = 962)²², SSZ-24 (Si/Al = 90)²³, HZSM-5 (Si/Al = 90) and TS-1 (Si/Ti = 45-300) zeolites were prepared by previous methods. The pore size of SSZ-31 (0.57 × 0.86 nm) is larger than that of TS-1 (0.54 × 0.56 nm). The pore of SSZ-24, classified as AFI type zeolite, (0.73 × 0.73 nm) is a one-dimensional straight channel. The sodium type zeolites were converted to the proton type by immersion in ammonium nitrate solution followed by calcination at 773 K for 5 h. The physical properties and acidity of the zeolites are listed in **Table 1**. The zeolite was compressed to small pellets and sieved from 32 to 48 mesh.

The rearrangement was carried out in a fixed bed reactor operated at atmospheric pressure. The zeolite fixed in the reactor was dried by carbon dioxide at 623 K for 1 h. CHO dissolved into methanol (50 mass%) was supplied by a microfeeder at constant flow rate to the evaporator. The vapor diluted with carbon dioxide (20 mol%) was fed to the reactor. The reactor effluent was collected at prescribed time intervals up to 2 h and then analyzed by a gas chromatograph equipped with a glass column (Shimadzu Corp., GC-8A, column length = 40 m).

The acidity and surface area of the used zeolite were measured to obtain information about catalyst deactivation. Furthermore, the coke content of the used zeolite was determined by thermal gravimetric balance. The surface area of the zeolite was obtained by the nitrogen adsorption method using a Belsorp 18 supplied by Nippon Bel Co., Ltd., in which the Langmuir equation was used for the calculations. The acidity and acid strength distribution were obtained from the ammonia TPD (temperature programmed desorption) method using a TPD-1-AT supplied by Nippon Bel Co., Ltd. The zeolite was placed in the cell for the TPD measurement and treated at 473 K for 2 h. Ammonia-diluted helium was passed through the cell at 373 K for a prescribed time. Helium was fed to the cell at the same temperature until no signal for ammonia from the mass detector was observed. The cell was heated from 373 to 873 K at 10 K/min. The relationship between the ammonia signal and temperature was recorded by a PC

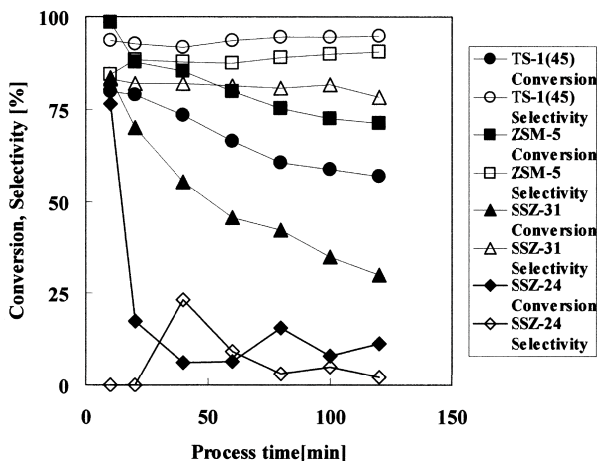


Fig. 1 Effect of Process Time on CHO Conversion and CL Selectivity

from the apparatus. The surface area and acidity of the used zeolites are listed in **Table 1**.

3. Results and Discussion

3.1. Effect of Type of Zeolite on CHO Conversion and CL Selectivity

Figure 1 shows the relationship between the CHO conversion, CL selectivity and process time (time on stream) over TS-1s (Si/Ti ratio = 45), SSZ-31 and SSZ-24 as well as ZSM-5 (Si/Al ratio = 90). The CHO conversion decreased with the process time, whereas the CL selectivity was almost constant. The deactivation was greater over SSZ-31 than TS-1 and ZSM-5 with the MFI structure. However, the deactivation over SSZ-24 was the highest among the zeolites. The CL selectivity over the MFI type zeolite exceeded 80%, whereas the selectivity over SSZ-31 was 80%. On the other hand, the selectivity over SSZ-24 was less than 30%. The Beckmann rearrangement over the HY type zeolite has very low CL selectivity and the catalyst deactivation is significantly greater than that over the MFI type zeolite²⁴. Since the acidity of the HY zeolite was higher than that of the MFI zeolite, high catalyst deactivation was considered to be responsible for the high concentration of acid sites. On the other

hand, the acid concentration of SSZ-24 was almost the same as those of TS-1 (Si/Ti = 90) and SSZ-31.

Catalyst deactivation of TS-1(45) was greater than that of TS-1(200). The conversion of CHO over TS-1s rapidly decreased with process time as the Si/Ti ratio decreased. Since the surface area was almost the same for all TS-1s, the difference in the catalyst deactivation should be responsible for the difference in the acidity. The acidity of the zeolite strongly affected the catalyst deactivation of the same type of zeolite. To improve the selectivity and catalyst deactivation, SSZ-24 was modified with platinum addition (0.5 wt%) as reported previously²⁰. This zeolite was called SSZ-24(Pt). The results of the Beckmann rearrangement over SSZ-24(Pt) are shown in Fig. 2. The CL selectivity and the catalyst deactivation were improved by the modification. The specific surface area decreased from 290 to 260 m²/g. The acidity of the original SSZ-24 was 0.022 mmol/g and the acidity of the Pt modified zeolite was 0.021 mmol/g. The mean pore diameter calculated from the surface area and pore volume was decreased by the modification, whereas the acidity did not change. Since the pore size of the SSZ-24(Pt) was decreased by the modification, the CL produced near the pore mouth was easily diffused to the entrance of the pore. As a result, the selectivity over SSZ-24(Pt) was higher than that over the original SSZ-24.

3. 2. Effect of Regeneration of Zeolite on Catalytic Activity

Figure 3 shows the effect of regeneration on CHO conversion and CL selectivity over the SSZ-31 zeolite

at 623 K. The used catalyst was regenerated with air or argon atmosphere at 673 K for 17 h. The regeneration was repeated 10 times. Thermal gravimetric analysis revealed that most of the coke or coke precursor deposited on the zeolite was removed under the conditions described previously²¹, even if the regeneration was carried out in the argon atmosphere. Although the conversion decreased with process time, the selectivity was almost constant in both atmospheres during the early regeneration. The initial conversion for each regeneration decreases with the repetition number. This result indicates that the concentration of active sites was decreased by the regeneration. A similar re-arrangement reaction by the regenerated SSZ-31 was

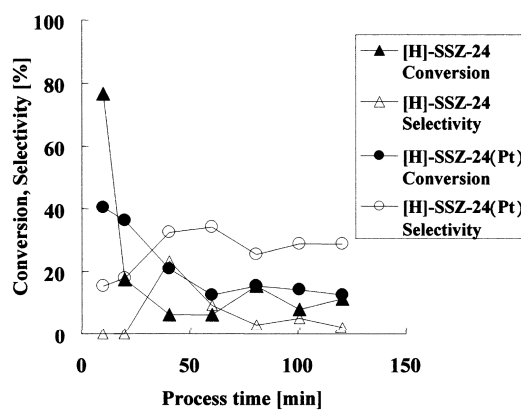


Fig. 2 Effect of Pt Modification on CHO Conversion and CL Selectivity over SSZ-24

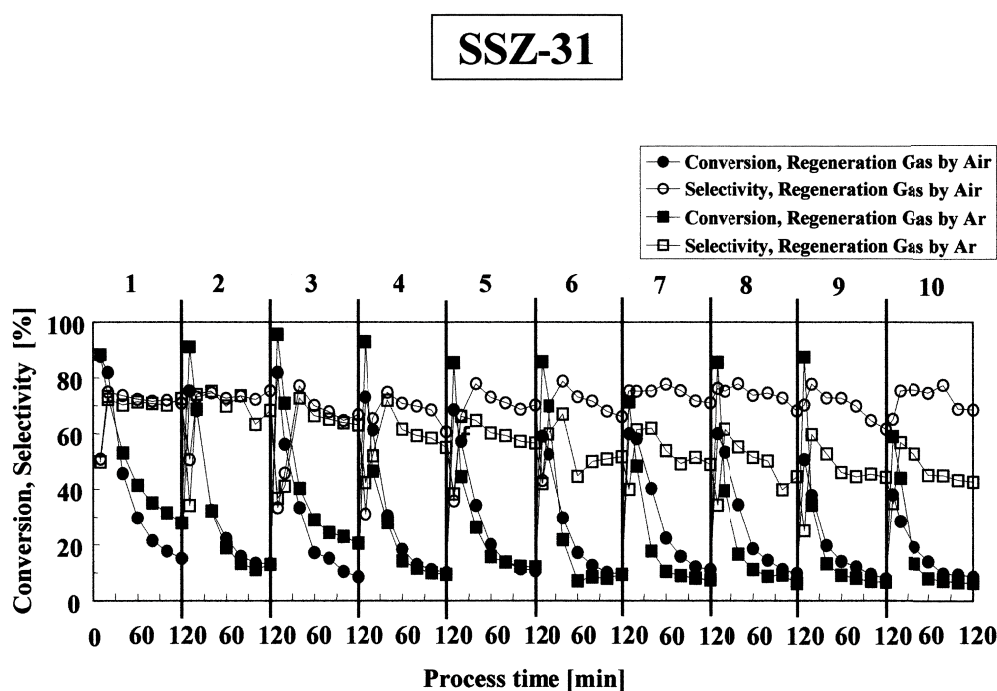


Fig. 3 Relationships between CHO Conversion, CL Selectivity and Number of Regenerations

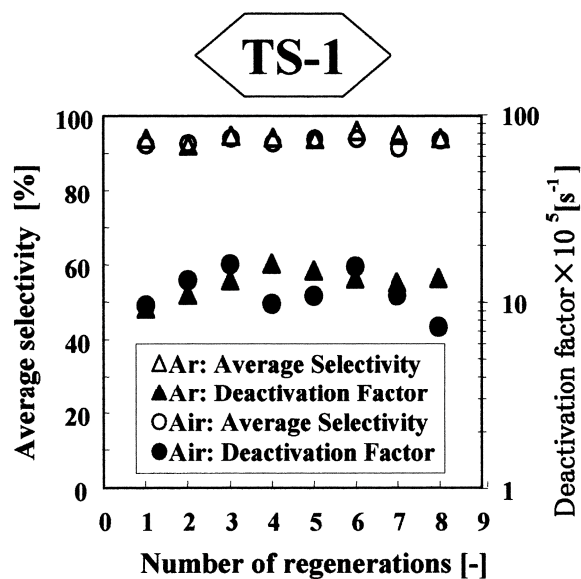


Fig. 4 Relationships between Average Selectivity, Deactivation Factor and Number of Regenerations (TS-1)

carried out over TS-1. However, rearrangement over the regenerated SSZ-24 was difficult as the CL selectivity was below 30% and the catalyst was rapidly deactivated after 3 regenerations.

To evaluate the catalytic activity, the rate constant was obtained from the conditions and CHO conversion. The mass balance equation for the fixed bed reactor is represented by Eq. (1). In Eq. (1), the first order reaction rate represents the disappearance of CHO.

$$W/F_{A0} = 1/(k \cdot C_{A0}) \cdot 1/\ln(1-x_A) \quad (1)$$

where, W is the mass of the catalyst [kg], F_{A0} is the molar rate [mol/s], k is the rate constant at any process time [$\text{m}^3/(\text{kg} \cdot \text{s})$], C_{A0} is the feed concentration of CHO [mol/m^3] and x_A is the CHO conversion [—]. Catalyst deactivation for the regeneration is represented by Eq. (2)¹⁹.

$$k = k_0 \cdot \exp(-b \cdot t) \quad (2)$$

where, k and k_0 are the rate constants at any process time and during the initial state without catalyst deactivation, respectively, b is the deactivation constant ($1/\text{s}$) and t is the process time [s].

Figures 4 and 5 show the effect of regeneration number on the average CL selectivity and deactivation constant over the regenerated TS-1 and SSZ-31, respectively. The regeneration was carried out in air and argon atmospheres. The average selectivity and catalyst deactivation constant did not change in any regeneration atmosphere over TS-1 as shown in Fig. 4. On the other hand, the CL selectivity over SSZ-31 regenerated in argon decreased with the regeneration number as shown in Fig. 5. However, the deactivation factor did not decrease with the regeneration number. These results suggest that silanol nests as the active sites for the rearrangement decreased with the regeneration

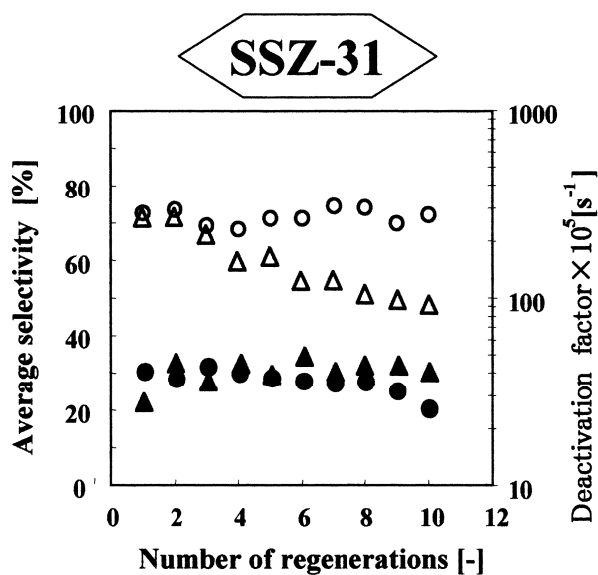


Fig. 5 Relationships between Average Selectivity, Deactivation Factor and Number of Regenerations (SSZ-31)

number. Table 2 lists the coke content, acidity and surface area of TS-1 and SSZ-31 after 10 regenerations in air and argon atmospheres. The coke content, acidity and surface area of SSZ-24 after 2 regenerations are also listed in Table 2. Although the physical properties shown in Table 2 were not different between the argon and air regenerations, the coke contents on SSZ-31 and SSZ-24 regenerated in the argon atmosphere were double or more compared to the air regeneration. Material deposited on HZSM-5 is easily removed by heating in an argon atmosphere or by heating at low temperature under vacuum conditions²¹. The deposited material is a coke precursor, such as an oligomerized caprolactam. On the other hand, material deposited on amorphous silica alumina catalyst was not removed in an argon atmosphere or during vacuum treatment. The material deposited on the silica alumina was believed to be hard coke. The materials deposited on SSZ-31 and SSZ-24 were hard coke.

3.3. Deactivation Mechanism for the Beckmann Rearrangement

Figure 6 shows the effect of the micropore size of the catalyst on the deactivation constant and coke content after the rearrangement. The results for H-mordenite²⁴, HZSM-5²⁴, HY²⁴ and amorphous silica alumina²¹ were obtained from our previous studies. Since the catalyst deactivation was affected by the acidity of the catalyst, the acidity was controlled from 0.01 to 0.02 mmol/g. The rearrangement was carried out at 573 K for 2 h under the previously described conditions. The catalyst deactivation and coke content suddenly increased with the micropore size up to 0.75 nm, such as for the SSZ-24 and HY type zeolites. The catalyst deactivation and coke content gradually decreased

Table 2 Effect of Regeneration on Coke Content, Acidity and Surface Area over TS-1, SSZ-31 and SSZ-24

(a) TS-1							
	Coke content [%]		Acidity [mmol/g]		Specific surface area [m ² /g]		
Regeneration gas	Air	Ar	Air	Ar	Air	Ar	
Fresh catalyst	–		0.004		400		
After reaction	10	8	0.003	0.003	330	290	

(b) SSZ-31							
	Coke content [%]		Acidity [mmol/g]		Specific surface area [m ² /g]		
Regeneration gas	Air	Ar	Air	Ar	Air	Ar	
Fresh catalyst	–		0.026		330		
After reaction	7.6	15.5	0.018	0.023	290	200	

(c) SSZ-24 (after 2 regenerations)							
	Coke content [%]		Acidity [mmol/g]		Specific surface area [m ² /g]		
Regeneration gas	Air	Ar	Air	Ar	Air	Ar	
Fresh catalyst	–		0.022		290		
After reaction	8.3	18.3	0.001	0.001	150	92	

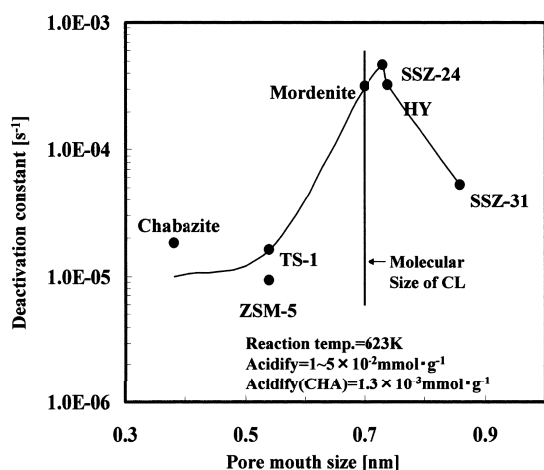


Fig. 6 Effect of Pore Size on Catalyst Deactivation over Zeolites

and remained almost constant beyond the maximum point. The catalyst deactivation constant for the amorphous silica-alumina (mean pore diameter = 3.0 nm) obtained by similar reaction conditions was $2.2 \times 10^{-5} \text{ s}^{-1}$. The constant was slightly smaller than that over SSZ-31. The effective molecular sizes of cyclohexanone oxime and ϵ -caprolactam were 0.65 and 0.75 nm, respectively, calculated from the HGS type molecular model. When the micropore size of the zeolite was similar to the molecular size of CHO and CL, the catalyst deactivation reached the maximum value.

CHO as the feed penetrated into the micropores of the zeolites. The CHO changed to CL, with molecular size slightly larger than that of CHO, over the active sites in the specified pore. As a result, the diffusion rate of CL was much smaller than that of CHO. This means that the residence time of CL in the pore is much longer than that of CHO. As a result, CL in the pore

changed to coke or oligomer as the precursor of the coke. On the other hand, when the rearrangement occurred over the MFI type zeolite, CHO could not penetrate into the pore, because the pore size is smaller than the molecular size of CHO. The rearrangement occurred on the outer surface over the MFI type zeolite. Furthermore, when the rearrangement occurred over the amorphous silica-alumina, with average pore size of 6 nm, the reaction mainly proceeded in the pores. However, CL could diffuse out from the large pores, whereas part of the CL changed to coke or its precursor.

These results indicate that when the rearrangement is carried out over zeolite with the same size micropores as the molecular size of CL, the catalyst deactivation is enhanced by the long residence time of the product. Although many catalysts have been applied to the Beckmann rearrangement, the lowest catalyst deactivation was obtained over the MFI type zeolites, such as ZSM-5 and TS-1. The product CL did not penetrate into the pores of the MFI zeolites. When the rearrangement was carried out over a proton exchanged ferrierite with pore size smaller than that of the MFI zeolite, the deactivation constant is similar to that of the MFI zeolite²⁵. On the other hand, when the rearrangement was carried out over a mesoporous material, such as MCM-41, the catalyst deactivation was greater than that of MFI zeolite, but lower than that of HY zeolite²⁶. These deactivation behaviors were explained by the pore sizes of the catalysts, if the acidity of the catalyst was 0.005 to 0.1 mmol/g.

The pore size of the catalyst is the most important factor to determine the selectivity of CL and catalyst deactivation for the Beckmann rearrangement of CHO.

4. Conclusions

The vapor phase Beckmann rearrangement of cyclohexanone oxime (CHO) was carried out over zeolites with different micropore sizes to elucidate the effect of pore size on the ϵ -caprolactam selectivity (CL) and catalyst deactivation rate. Catalyst deactivation was strongly dependent on the micropore size of the catalyst. When the micropore size of the catalyst was similar to the molecular size of CHO or CL, the maximum deactivation rate was observed. This behavior could be explained by the fact that CHO penetrated into micropores similar to the molecular size, where the CHO reacted with CL in the pore. Since the molecular size of CL is larger than that of CHO, the diffusion rate is significantly lower. As a result, the product CL changed to coke or its precursor. Since the pore size of SSZ-24 is similar to the molecular size of CL, the deactivation rate was higher than those of SSZ-31 and TS-1.

Catalyst deactivation for the vapor phase Beckmann rearrangement is determined by the relationship between the pore size of the zeolite and the molecular size of CL.

Acknowledgments

This study was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Specially Promoted Research, 13126101, 2004.

References

- 1) Sato, H., Hirose, K., Kitamura, M., *Nippon Kagaku Kaishi*, **1989**, 548 (1989).
- 2) Roeseler, J., Heitmann, G. P., Hoelderich, W. F., *Appl. Catal. A: General*, **144**, 319 (1996).
- 3) Komatsu, T., Maeda, T., Yashima, T., *Microporous Mesoporous Mater.*, **35/36**, 173 (2000).
- 4) Thangral, A., Sivasanker, S., Ratnasamy, P., *J. Catal.*, **137**, 252 (1992).
- 5) Tatsumi, T., Dai, L. X., Proceedings of 12th Inter. Zeolite Conference, Vol. II, 1998, p. 1455.
- 6) Zhang, Y. J., Wang, Y. Q., Bu, Y. F., Mi, Z. T., Wu, W., Min, E., Han, S., Fu, S. B., *Catal. Commun.*, **6**, 53 (2005).
- 7) Singh, P. S., Bandyopadhyay, R., Hedge, S. G., Rao, B. S., *Appl. Catal. A: General*, **136**, 249 (1996).
- 8) Shouro, D., Moriya, Y., Nakajima, T., Mishima, S., *Appl. Catal. A: General*, **198**, 275 (2000).
- 9) Kim, S. J., Jung, K. D., Joo, O. S., Kim, E. J., Kang, T. B., *Appl. Catal. A: General*, **266**, 173 (2004).
- 10) Immuel, O., Schwarz, H. H., Starcke, H., Swoden, W., *Chem.-Ing.-Tech.*, **56**, 612 (1984).
- 11) Sato, S., Urabe, K., Izumi, Y., *J. Catal.*, **102**, 99 (1986).
- 12) Sato, S., Hasebe, H., Sakurai, S., Urabe, K., Izumi, Y., *Appl. Catal.*, **29**, 107 (1987).
- 13) Mao, D. S., Lu, G. Z., Chen, Q. L., *Appl. Catal. A: General*, **279**, 145 (2005).
- 14) Ushikubo, T., Wada, K., *J. Catal.*, **148**, 138 (1994).
- 15) Heitmann, G. P., Dahlhoff, G., Hoelderich, W. F., *J. Catal.*, **186**, 12 (1999).
- 16) Heitmann, G. P., Dahlhoff, G., Niederer, J. P. M., Hoelderich, W. F., *J. Catal.*, **194**, 122 (2000).
- 17) Ishida, M., Suzuki, T., Ichihashi, H., Shiga, A., *Catal. Today*, **87**, 187 (2003).
- 18) Ichihashi, H., Kitamura, M., *Catal. Today*, **73**, 23 (2002).
- 19) Takahashi, T., Nasution, M. N. A., Kai, T., *Appl. Catal. A: General*, **210**, 339 (2001).
- 20) Takahashi, T., Kai, T., *J. Jpn. Petrol. Inst.*, **47**, (3), 190 (2004).
- 21) Takahashi, T., Kai, T., Nakao, E., *Appl. Catal. A: General*, **262**, 137 (2004).
- 22) Bandyopadhyay, R., Ahedi, R. K., Kubota, Y., Ogawa, M., Goto, Y., Fukushima, Y., Sugi, Y., *J. Mater. Chem.*, **11**, 1869 (2001).
- 23) Lobo, R. F., Davis, M. E., *Microporous Materials*, **3**, 61 (1994).
- 24) Takahashi, T., Ueno, K., Kai, T., *Shokubai*, **31**, 365 (1987).
- 25) Yashima, T., Miura, K., Komatsu, T., *Stud. Surf. Sci. & Catal.*, **84**, 1897 (1994).
- 26) Tsai, C. C., Zhong, C. Y., Wang, I., Liu, A. B., Chen, W. H., Tsai, T. C., *Appl. Catal. A: General*, **267**, 87 (2004).

要 旨

ゼオライトによる気相バックマン転位反応の活性劣化に及ぼす細孔径の影響

高橋 武重, 仲西 真由美, 甲斐 敬美

鹿児島大学工学部応用化学工学科, 890-0065 鹿児島市郡元1-21-40

シクロヘキサノンオキシムの気相バックマン転位反応において触媒活性劣化に及ぼす細孔径の影響を明らかにするため、MFI構造をもつTS-1およびこれよりも大きな細孔をもつSSZ-31およびSSZ-24を触媒として反応を行った。SSZ-24を用いたときの活性劣化定数は、本研究で使用したゼオライトの中で最大になった。さらに、 ϵ -カプロラクタムの分子径/ゼオライトの細孔径比が1になるとき、同程度の酸性度をもつゼオラ

イト間で最大の活性劣化因子をもつことが分かった。これらの結果は、細孔内の活性点で生成した ϵ -カプロラクタムが細孔から拡散できないため、 ϵ -カプロラクタムが長時間にわたり細孔内に滞留し、結果としてコークあるいはその前駆体になったことを示唆している。ゼオライトの細孔径はバックマン転位反応の活性劣化に大きな影響を与えた。

.....